N69-40977

NASA TECHNICAL MEMORANDUM

NASA TM X-52697

NASA TM X-52697

OBSERVATIONS OF HOTSPOTS AND METALLIC DEPOSITS IN CdS THIN FILM SOLAR CELLS

by Michael P. Godlewski, John M. Bozek, and Larry R. Scudder
Lewis Research Center
Cleveland, Ohio

October 10, 1969

E-5347

This information is being published in prelimi-
nary form in order to expedite its early release.

OBSERVATIONS OF HOTSPOTS AND METALLIC DEPOSITS IN CdS THIN FILM SOLAR CELLS

by

Michael P. Godlewski, John M. Bozek, and Larry R. Scudder

Lewis Research Center
Cleveland, Ohio

ABSTRACT

The output of thin film CdS solar cells degraded while illuminated at open circuit and while unilluminated at forward bias. Hotspots appeared at grid wires. During the illuminated tests copper nodules formed on the surface and within the cell. Surface nodules coincided with hotspots only when they contacted grid wires; subsurface nodules were found only under grid wires and coincided with hot spots. In the unilluminated tests copper filaments were found under grid wires at hotspot locations and extended through the cell to the substrate.

OBSERVATIONS OF HOTSPOTS AND METALLIC DEPOSITS IN CdS THIN FILM SOLAR CELLS

by Michael P. Godlewski, John M. Bozek
and Larry R. Scudder

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

E-5347

SUMMARY

The output of thin film CdS solar cells degraded while illuminated at open circuit and while unilluminated at forward bias. Hotspots appeared at grid wires. During the illuminated tests copper nodules formed on the surface and within the cell. Surface nodules coincided with hotspots only when they contacted grid wires; subsurface nodules were found only under grid wires and coincided with hot spots. In the unilluminated tests copper filaments were found under grid wires at hotspot locations and extended through the cell to the substrate.

INTRODUCTION

CdS thin-film solar cells degrade in their photovoltaic characteristic in simulated space environment (ref. 1). In order to better identify the causes of this photovoltaic degradation, a number of CdS thin-film solar cells have been tested under a variety of conditions.

Previous work has shown that cells tested under constant illumination while loaded at open circuit voltage showed a degradation of photovoltaic characteristics, which was different from that observed in the simulated space environment tests. The constant illumination tests also showed the existence of nonuniform temperature distributions (hot spots), and metallic

TM X-52697

deposits on the surface of the CdS cell (refs. 2 and 3). Shorting paths have been observed beneath the metallic deposits and are thought to be the cause for the photovoltaic degradation (private communication from Lee Shiozawa, Clevite Corp.). An additional clue to the composition of these metallic deposits is in the early literature (ref. 4) where it was shown that copper deposits formed in copper sulfide rectifiers.

One object of the work reported here was to further investigate the nature of hot spots and metallic deposits that occur on CdS thin-film solar cells. Cells were degraded, while open-circuited, under constant illumination and while forward-biased in the dark. The metallic deposits and hot spots that formed were examined with photomicrographs, electron microprobe analysis, x-ray diffraction and preferential etching. Metallic deposits were also grown on the surface of ungridded cells using gold point electrodes.

EXPERIMENT DESCRIPTION

CdS Thin-Film Solar Cells

Commercial and Lewis Research Center experimental thin-film CdS solar cells are shown in Figure 1. The commercial cells use a metallized plastic substrate and gold-filled epoxy to bind the gold-plated copper grid to the cell surface (ref. 5). The Lewis Research Center cell differs in construction, using molybdenum as a substrate and a cover plastic with nylon adhesive to hold down the grid. Grids on the Lewis Research Center cells were gold-plated copper or solid gold. In some of the tests described below, both commercial and Lewis Research Center cells without grids or cover plastics were used.

Constant Illumination, Open Circuit Tests

In these tests five cells, commercial and Lewis Research Center type, were loaded at open circuit while under constant illumination for about 100 hours. A tungsten lamp adjusted to an intensity of approximately 136 mw/cm^2 was used in these tests. The cells were mounted on a water-cooled aluminum block. The cell temperature was monitored by a thermocouple mounted on the cover plastic and ranged from 30° C to 50° C. The photovoltaic I-V characteristics of cells were taken before and after exposure to monitor the photovoltaic degradation.

Dark Forward and Reverse Bias Tests

A commercially available cell was forward biased (grid side positive) in the dark. The dark forward diode characteristic was periodically monitored to determine the extent of electrical degradation of the cell. About one ampere applied for about five minutes was sufficient to induce degradation. After the cell degraded it was placed in a reverse bias mode (about 0.5 V and 1.0 amp) to induce recovery of dark characteristics.

Dark Forward and Reverse Bias Tests with Point Contacts

Attempts were made to grow metallic deposits under point contacts on the surface of unilluminated cells which had no grids and no cover plastics. Solid gold point contact electrodes were used to make electrical contact to the cell surface and to the substrate tab. A constant forward or reverse bias voltage was applied to these point electrodes and the current monitored.

In the reverse bias mode the voltages varied from 0.35 V to 0.38 V to 2.5 volts. These voltages were applied for periods of 1000 hours, 170 hours and 24 hours, respectively. In the forward bias mode a constant voltage of 1.5 volts was applied over a period of 72 hours. The current passing through the point contacts was continuously monitored.

OBSERVATION TECHNIQUES

Nonuniform Cell Temperature Distribution

Nonuniform temperature distribution, commonly called hot spots, on the cell surface of CdS solar cells were detected by an electronic infrared sensing device (ref. 6). To further isolate these hot spots and also detect hot spots on other parts of cell other than its active surface, cholesteric-type liquid crystals (ref. 7) sensitive in the 30° C to 32° C range were used.

Photomicrographs

Using the techniques described in ref. 8, various samples of cells subjected to tests described above, were cross sectioned. Some samples were prepared with electrical leads accessible for biasing. The temperature pattern of these latter samples was determined by applying liquid crystals to the polished cross sectioned surfaces while the cells were forward biased.

Photomicrographs were taken and the temperature distribution monitored with liquid crystals after each removal of 0.4 mils (10 μm) from the cross section.

Material Identification

In order to identify the metallic deposits on and in CdS solar cells which have been subjected to tests discussed previously, three analytical tools were used. The first is an electron microprobe analysis. This technique identifies elemental substances in polished samples by detection of characteristic x-rays resulting from high energy electron excitation. The second tool is x-ray diffraction. In this method, the composition of samples is determined by analysis of scattered x-ray intensities. The third method, which is the least exact, is preferential etching. Polished samples are etched with different etchants and microscopically examined. The etches used here to identify CdS and copper were 15 percent HCl solution and a solution of five parts NH_4OH, five parts H_2O, two parts H_2O_2, respectively. Aqua Regia was used as an etch for gold.

RESULTS

Constant Illumination, Open Circuit Tests

A total of five commercial and Lewis CdS thin-film solar cells were tested at a constant illumination of approximately air-mass-zero intensity. All cells were loaded at open circuit. Within 100 hours after being placed on test, the photovoltaic characteristics degraded. Hot spots and metallic deposits in nodule form appeared on the surface of the cell. The top view of a typical nodule is shown in figure 2.

A cross-section photomicrograph of a piece of a commercial cell containing a nodule is shown in figure 3. The nodule, resting on the surface of the sulfide adjacent to the gold-plated copper grid, has pushed up the cover plastic. An electron microprobe analysis identified the nodule as elemental copper. Subsequently, a nodule was removed from the surface of the cell, and x-ray diffraction analyses confirmed that the nodule was copper. Preferential etching with a copper etch also showed many other nodules to be copper.

The number of nodules formed and their location varied from cell to cell. Usually, at least one, and occasionally clusters of up to 40 nodules appeared. The clusters of nodules were typically grouped over an area of about 20 cm^2 near the periphery of a cell.

All cells developed hot spots, detected by liquid crystals, as shown in figure 4. The hot spots were found to coincide with a grid wire. Close examination with a microscope of two hot spots revealed that nodules were present and that these nodules were in contact with a grid wire. A cross-section photomicrograph of another hot spot that appeared during this test is shown in figure 5. Two large copper inclusions are seen in the shattered CdS under the grid.

No difference in nodule growth or hot spot formation was observed that could be ascribed to substrate or grid material. Comparable results were obtained on cells with molybdenum or zinc-silver substrates or with solid gold and gold-plated copper grids.

Unilluminated Forward and Reverse Bias Tests

Forward biasing of an unilluminated CdS solar cell for a few minutes caused a number of hot spots on the surface of the cell similar to that shown in figure 4. In an effort to remove these hot spots formed by forward bias, the cell was reverse biased to about 0.5 volt. While under reverse bias one of the hot spots was seen to disappear.

A portion of the cell, about 2 $in.^2$ (6.5 cm^2), containing an active hot spot and the above discussed deactivated hot spot was then cross sectioned. The active hot spot similar to the one shown in figure 4 was also observed with liquid crystals on the polished cross section surface while the cell was forward biased. However, continued polishing caused this hot spot to disappear. A photomicrograph of a subsequent cross section of that area of the cell is shown in figure 6. The lamellar crack in the CdS portion of the cell shown in figure 6 was caused and propagated by the constant flexing of the cell during handling of the cell sample while a large number of polishes were made. It is believed that the propagation of the lamellar crack severed the filament as shown in figure 6 leading to the abrupt disappearance of the hot spot.

Lapping and polishing of cross sections was done in the region of the deactivated hot spot also. A cross section photomicrograph of this region is presented in figure 7. Comparison of this region with the region of an active hot spot shown in figure 6 reveals sharp differences. In figure 7, the cavity in the CdS contains unidentified silvery colored mounds. Note also, the fine grained CdS surrounding the small coppery inclusions at the crater side. The presence of such a localized disordered region can be the result of a very high temperature process. A likely process would be the fusing of a copper filament, like the one shown in figure 6, under strong reverse bias. The destruction of this filament, if it is a shorting path, then would account for the observed disappearance of the hot spot.

In contrast to the results obtained under constant illumination, a visual scan of the cell surface with a 60X microscope revealed no nodules.

Unilluminated Reverse Bias with Point Contacts

Copper deposits in dendritic form appeared under the point contact of unilluminated reverse-biased ungridded, uncovered commercial and Lewis Research Center cells. Initial current levels for various applied voltages were in the milliampere range, but increased significantly during the bias periods.

Dendritic copper deposits appeared on the copper sulfide under the point contacts, for the reverse bias values of 2.5 and 0.38 volts. No copper was seen at a 0.35 volt reverse bias.

Figure 8 shows a copper dendrite which appeared for the 2.5 volt case. The elliptical discolored area seen on the copper sulfide surface was typical of dendrite formation areas. Cross sectioning through a dendrite showed the copper only on the surface penetration of the dendrite into the CdS film was not observed.

Unilluminated Forward Bias with Point Contacts

During a 70 hour unilluminated forward bias test, the current passing through the uncovered cell increased substantially. At the conclusion of the test a discoloration was noticed on the copper sulfide surface. It was similar to the discoloration noted in the copper dendrite growth process but much smaller.

Cross sectioning the region of cell directly under the point contact revealed no metallic deposits.

SUMMARY OF RESULTS

Examination by photomicrography, electron microprobe and x-ray diffraction analysis and chemical etching of hot spots and metallic deposits that developed on CdS thin film solar cells under a variety of test conditions yielded the following results:

1. During constant illumination tests, nodules of metallic copper formed on the surface of the cells. Most of these nodules did not act as hot spots. Hot spots resulted from copper nodules touching or growing under a grid wire, however. Hot spot and nodule formation did not appear to be altered by changing grid or substrate material.
2. Under forward bias in the dark, hot spots formed and were accompanied by copper filaments extending from a grid wire to the substrate of the cell. In contrast to the illuminated test, no surface nodules were observed using a 60X microscope. Reverse bias in the dark resulted in the elimination of the hot spots. High current flow through the copper filament apparently led to its destruction.
3. When ungridded cells were reverse-biased using solid gold point probes, copper dendrites were grown on the surface of the cell. No growth was seen under forward bias.

REFERENCES

1. Kennerud, K. L.: Simulated Space Environmental Tests on Cadmium Sulfide Solar Cells. Rep. D2-121002-1, Boeing Co. (NASA CR-72507), Feb. 28, 1969.

2. Scudder, Larry S.; Godlewski, Michael P.; and Klucher, Thomas M.: Observations on Degraded CdS Solar Cells. NASA TM X-52668.

3. Shirland, F. A.; Bower, W. F.; Dunn, W. F.; and Green, J. B.: CdS Solar Cell Development. Clevite Corp. (NASA CR-72534), Mar. 14, 1969.

4. Paulowski, Franz: Current Rectifier. Patent No. 830, 924, United States, Sept. 11, 1906.

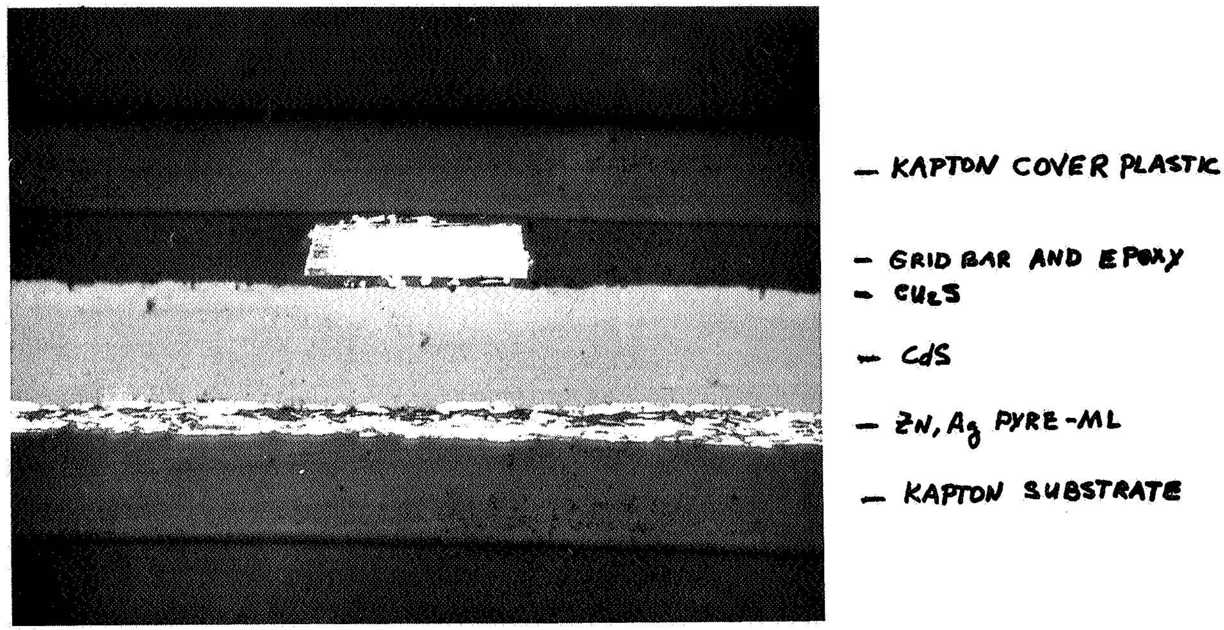
5. Shirland, F. A.; Bower, W. F.; and Green, J. R.: CdS Solar Cell Development. Clevite Corp. (NASA CR-72382), Feb. 29, 1968.

6. Borg, Sven-Bertil: Thermal Imaging with Real Time Picture Presentation. Appl. Opt., vol. 7, no. 9, Sept. 1968, pp. 1697-1703.

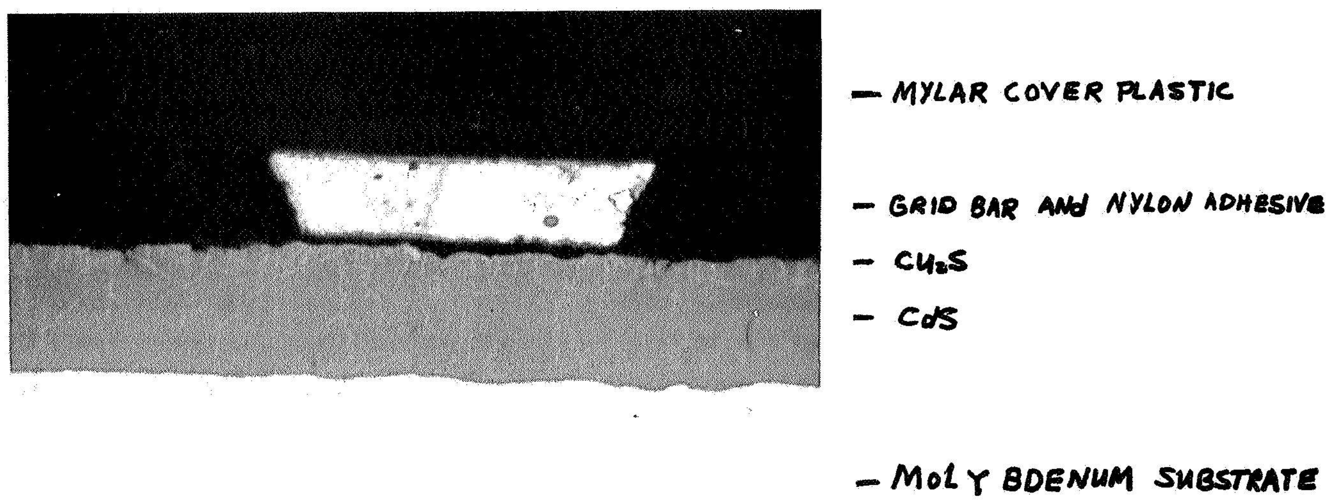
7. Fergason, James L.: Liquid Crystals in Nondestructive Testing. Appl. Opt., vol. 7, no. 9, Sept. 1968, pp. 1729-1737.

8. Bozek, John M.: Effects of Sample Preparation on Photomicrographs of Cadmium Sulfide Thin-Film Solar Cells. NASA TM X-1722, 1969.

E-5347



a. 500X



b. 600X

FIGURE 1 CROSS-SECTION PHOTOMICROGRAPHS OF (a) commercial AND (b) Lewis CdS SOLAR CELLS

E-5347

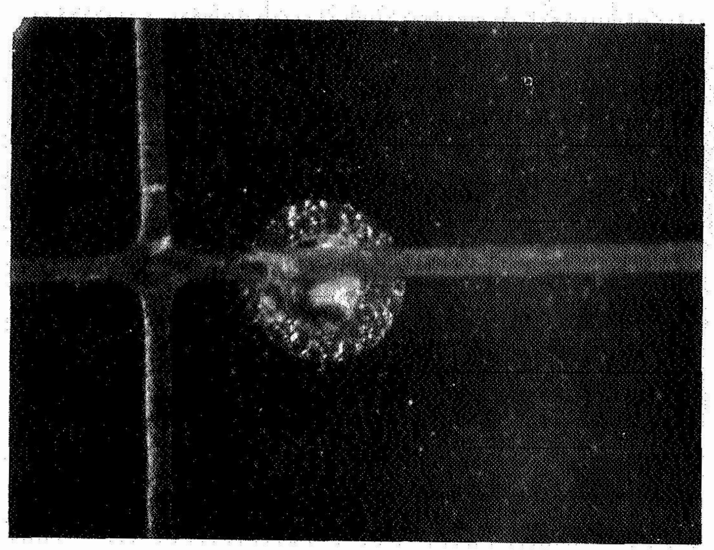


FIGURE 2 NODULE FORMED ON LEWIS CELL DURING CONSTANT ILLUMINATION, OPEN CIRCUIT VOLTAGE TEST.—210X

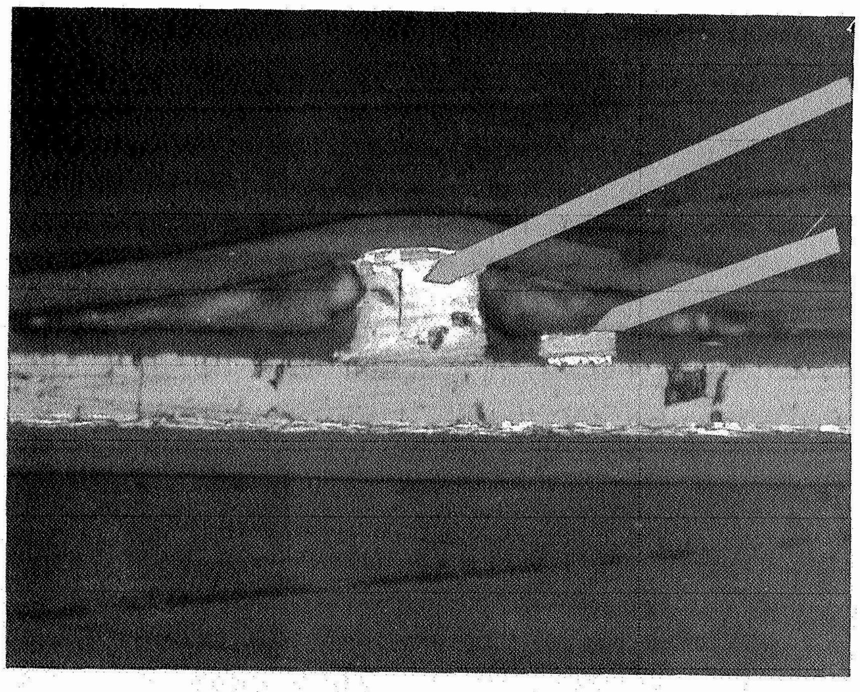


FIGURE 3 CROSS SECTION PHOTOMICROGRAPH OF CdS CELL SHOWING A NODULE. 250X

E-5347

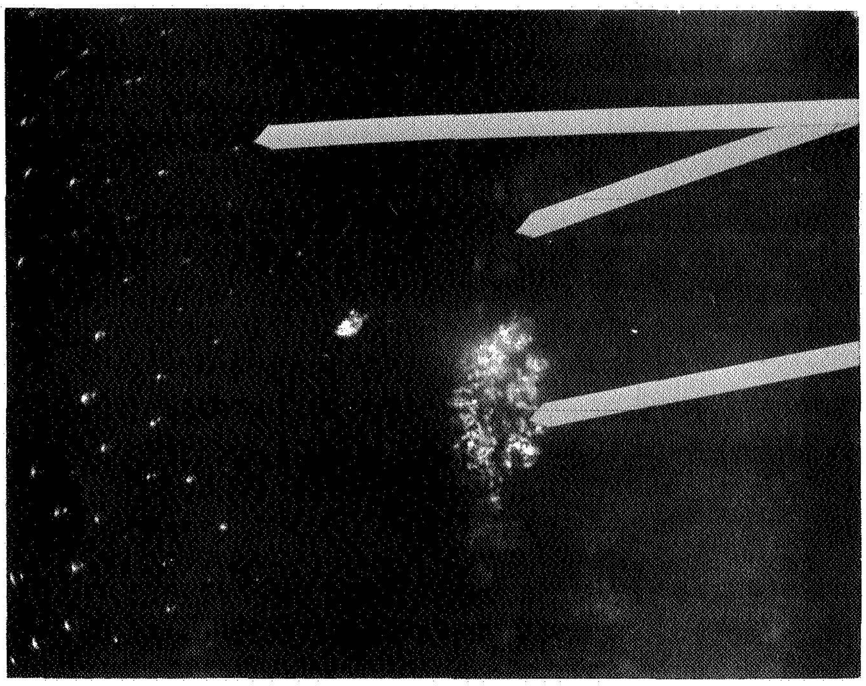


FIGURE 4 HOTSPOT APPEARING ON CELL COATED WITH LIQUID CRYSTALS. 200X

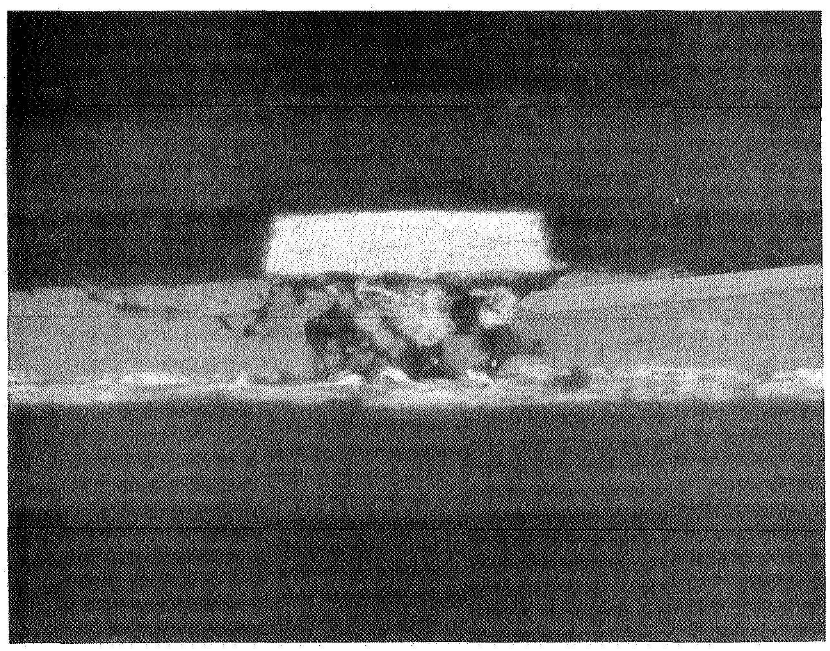


FIGURE 5 INCLUSIONS FOUND IN HOTSPOT REGION FORMED DURING CONSTANT ILLUMINATION TESTING 500X

E-5347

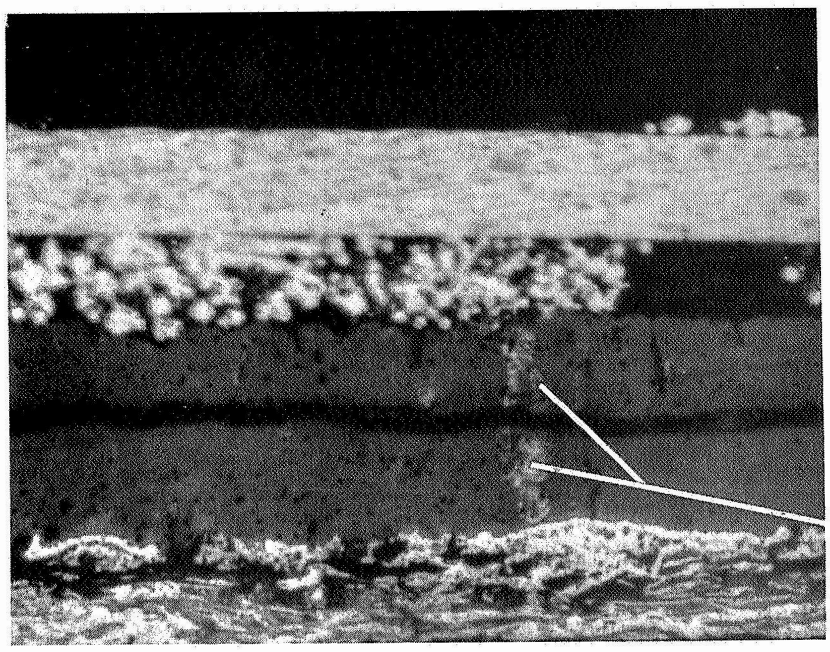


FIGURE 6 CROSS SECTION OF COPPER FILAMENTS IN CdS SOLAR CEll. 1000X

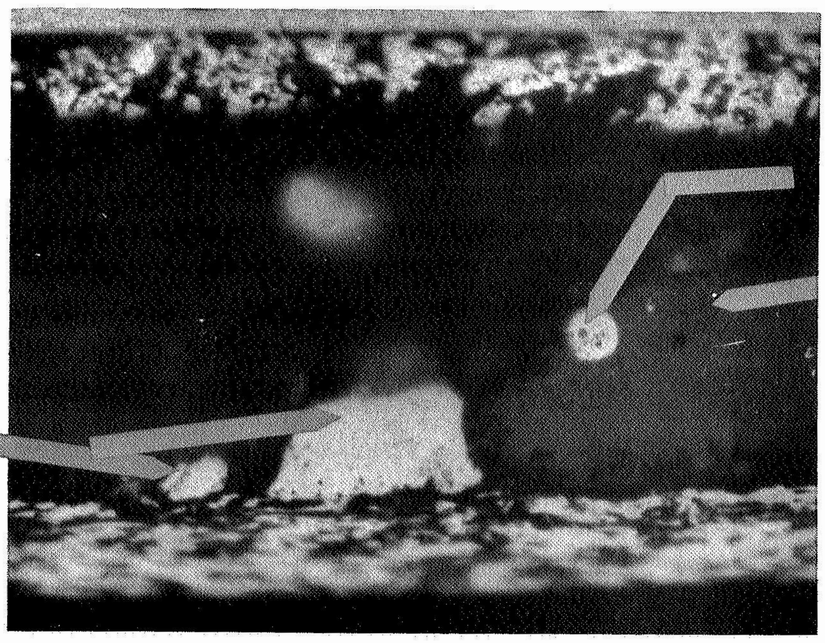


FIGURE 7 CROSS SECTION OF HOTSPOT REGION INACTIVATED BY REVERSE BIAS. 1000X

E-5347

FIGURE 8 DENDRITE ON Cu_2S
SURFACE GROWN WITH 2.5 volt
REVERSE BIAS. ~ 40X